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**PARTICLE SIZE DISTRIBUTIONS DURING DIFFUSION
CONTROLLED GROWTH AND COARSENING
(PREPRINT)**

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14. ABSTRACT The chemical partitioning of alloying elements between the disordered γ and ordered γ' phases in the nickel base superalloy Rene 88DT, has been characterized in detail using three dimensional atom probe tomography (3DAP) coupled with energy-filtered transmission electron microscopy studies. After a homogenization treatment followed by a water quench, it is observed that the morphology of the γ' precipitates remains near-spherical even after long aging times. Compositional variation, observed between small (<5 nm) and larger γ' precipitates, reduces with increasing aging time, while the compositional gradient across the γ/γ' interface decreases. The process of growth of γ' precipitates seems to occur through coalescence of adjacent γ' precipitates, facilitated through the formation of "necks" between adjacent precipitates. These necks are observed to have intermediate elemental concentration values, between the matrix and the γ' precipitate compositions.					
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Particle Size Distributions during Diffusion Controlled Growth and Coarsening

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ABSTRACT

Theoretical analysis of particle growth and coarsening conducted in the present work, which includes stochastic flux of a solute inside/from the growing particles, predicts normal distribution of the particle sizes, independent on the particle volume fraction. This result agrees well with the numerous experimental data and it solves a mysterious problem related with a non-symmetrical size distribution in earlier Lifshitz-Slyozov-Wagner theory.

INTRODUCTION

Growth and coarsening of second phase particles in a supersaturated solution are important parts of phase transformations which tune various physical, chemical and mechanical properties of materials. These transformation processes occur when the nucleation stage of the second phase particles has completed and further decrease in the free energy of the system is mainly due to a decrease in the total interfacial energy. The particle growth originates from supersaturation, which is still present in the system after completion of the nucleation stage, and from the concentration gradients around the particles of different sizes caused by the capillary effect (the Gibbs-Thomson equation), which result in preferential growth of larger particles and shrinkage of smaller particles and in a continuous increase in the particle average size [1,2]. The major advance for the theoretical description of this process was made by Lifshitz, Slyozov and Wagner (so called LSW theory) [3,4]. This theory describes very well evolution of averaged growth parameters, such as the average radius, \bar{r} , and the number density of the particles, N , with time t . For example, for the diffusion controlled growth process, the LSW theory predicts the following behavior:

$$\bar{r}^3 - \bar{r}_0^3 = K_{\text{LSW}} t \quad (1)$$

$$N^{-1} - N_0^{-1} = (4\pi/3f_v) K_{\text{LSW}} t \quad (2)$$

where \bar{r}_0 and N_0 are the average radius and the number density of particles at time $t = 0$, f_V is the particle volume fraction and K_{LSW} is the rate constant, which is given by:

$$K_{LSW} = \frac{8\gamma D V_m c_\infty}{9RT} \quad (3)$$

In Equation (3), γ is the particle-matrix interface energy, D is the diffusion coefficient, V_m is the molar volume of the second phase and c_∞ is the equilibrium saturated concentration of the alloying element in the matrix at the temperature T , and R is the gas constant. Many experimental results on the particle growth and coarsening indeed follow these relationships. However, the LSW theory leads to a highly asymmetric particle size distribution (PSD):

$$\Phi_{LSW} = \left(\frac{3}{3+\rho} \right)^{7/3} \left(\frac{3}{3-2\rho} \right)^{11/3} \exp\left(\frac{-2\rho}{3-2\rho} \right) \text{ at } r < 1.5 \bar{r} \text{ and } \Phi_{LSW} = 0 \text{ at } \rho > 1.5 \quad (4)$$

with a sharp cutoff near the particle radius $r = 1.5 \bar{r}$, which virtually does not agree with any experimentally reported particle size distributions [2,5]. The reported distributions are generally broader and more symmetric than the LSW prediction (Figure 1).

A major problem with the LSW theory is believed [1,2] to be due to using the mean field approximation for the kinetic equation. This approximation assumes that the growth of a particle does not depend on diffusional interactions between nearest particles and it does not take into account the effect of the volume fraction of particles on the rate of growth of these particles. After taking into account the volume fraction of the particles and their soft interactions, modified LSW theories [6,7,8,9, see also ref. 2 for review] made the rate constant in Equation (1) dependent on the particle volume fraction and improved PSDs by making them broader and more symmetric. However, these modified PSDs become near symmetrical only at high particle volume fractions ($f_V > 0.1$) [2]. The fact that experimental PSDs are also symmetric at very low f_V may indicate that some other quantity or condition of the system, which has not been taken into account in the particle growth theories, is responsible for the near-symmetric distribution. In this paper we will show that the missed link between experimental and theoretical PSDs was stochastic solute diffusion that was not taken into account in those theories. To derive the PSD for the growth and coarsening process, we use a classic approach developed by Einstein more than 100 years ago when he solved the problem of Brownian motion [10].

ANALYSIS

Here we consider diffusion-controlled growth and coarsening of second phase spherical particles in a supersaturated solution, although similar approach can also be applied to the reaction-limited growth. The particles are distributed by their sizes (radii) and their number density is N , which are time dependent. The initial concentration of the solute element in the solution is c_o , current concentration is c , and its concentration in particles is assumed to be constant and equal c_p . In general case, growth of these particles is due to (a) the diffusion current of solute across the particle/matrix interface caused by the solute concentration gradients near the particles and (b) stochastic diffusion of solute across the interface through the Brownian motion. The first process was well described in the previous theories, while the second process was ignored. If this stochastic process is taken into account, the diffusion current, J , of solute across the particle/matrix interface per unit area and the rate of particle growth, dr/dt , are given:

$$J = D \left. \frac{dc}{dR} \right|_{R=r} + g(r,t)\xi(t) \quad (5)$$

$$\frac{dr}{dt} = \frac{2\gamma\Omega D c_\infty}{r c_p k T} \left(\frac{1}{r_c} - \frac{1}{r} \right) + g(r,t)/c_p \xi \quad (6)$$

Here R is the distance from the center of a particle of radius r , γ is matrix/particle interface energy, Ω is the particle atomic (or molar) volume, r_c is a critical radius, given by a linearized Gibbs-Thompson equation, $c = c_\infty \left(1 + \frac{2\gamma\Omega}{r_c k T} \right)$, at which a particle of radius r_c is in equilibrium with the solution of concentration $c(t)$, c_∞ is the equilibrium solute concentration (at $t \rightarrow \infty$), t is time, k is the Boltzmann constant (or universal gas constant), T is the absolute temperature, $g(r,t)\xi$ is a Langevin (stochastic) flux, and ξ is the rapidly fluctuating random term, which has the following properties [11,12]:

$$\langle \xi(t) \rangle = 0 \text{ and } \langle \xi(t) \xi(t') \rangle = \delta(t-t') \quad (7)$$

Conditions (7) indicate that the average stochastic flux is equal zero, while its correlation function is non-zero and all the fluctuations at different times are independent. In equation (7), $\langle \rangle$ means the mean value and δ is a delta function. Because of the stochastic nature of $g(r,t)\xi(t)$, this value should not affect the time dependences of the average values of radius, number density and volume fraction of the growing particles. However, the presence of the stochastic flux will change the particle size distribution, as it is shown below.

In the presence of the diffusion current, Equation (5), the radius r of an individual particle during a very short period of time, $d\tau$, will increase by the amount of Δ , which can be defined from Equation (6) as:

$$\Delta = \frac{2\gamma\Omega Dc_\infty}{rc_p kT} \left(\frac{1}{r_c} - \frac{1}{r} \right) d\tau + g(r,t)/c_p dW(t) \quad (8)$$

where $W(t) = \int_0^t \xi(t)dt$ is the Wiener process, which, in Ito calculus for stochastic processes, has

the following properties: $d\tau dW(t) = 0$ and $[dW(t)]^2 = d\tau$ [12]. For each particle, Δ has a different (positive or negative) value and the number of the particles, dN , which radius escalations are between Δ and $\Delta+d\Delta$, is given by

$$dN = N\phi(\Delta)d\Delta \quad (9)$$

where the function $\phi(\Delta)$ is only different from zero for very small values of Δ and satisfies the

condition $\int_{-\infty}^{\infty} \phi(\Delta)d\Delta = 1$. If only stochastic flux, $g(r,t)\xi$, were present, then $\phi(\Delta) = \phi(-\Delta)$.

However, the presence of a directional flux due to the concentration gradient (Equation 5) is the main contributor to the particle growth and, therefore, $\phi(\Delta) \neq \phi(-\Delta)$.

We now define a distribution function $\Phi(r,t)$ as a number of particles per unit volume of radius r at time t . Equation (9) allows us to determine the distribution of particles at time $t + d\tau$ from the distribution at time t . Indeed, the number of particles at time $t + d\tau$ that have radii between r and $r + dr$ is:

$$\Phi(r,t+d\tau)dr = dr \int_{-\infty}^{\infty} \Phi(r - \Delta, t)\phi(\Delta)d\Delta \quad (10)$$

Since $d\tau$ and Δ are very small, we can set Taylor series:

$$\Phi(r, t + \tau) = \Phi(r, t) + (d\tau) \frac{\partial \Phi(r, t)}{\partial t} \quad (11)$$

$$\Phi(r - \Delta, t) = \Phi(r, t) - \Delta \frac{\partial \Phi(r, t)}{\partial r} + \frac{\Delta^2}{2} \frac{\partial^2 \Phi(r, t)}{\partial r^2} \quad (12)$$

We left the third term in Equation (10) because Δ contains the Wiener process (see Equation 8) and, therefore, $\Delta^2 = (g/c_p)^2 (d\tau)$. We can use Equation 12 under the integral, because only small values of Δ contribute to Equation 10:

$$\Phi(r, t) + (d\tau) \frac{\partial \Phi(r, t)}{\partial t} = \Phi(r, t) \int_{-\infty}^{\infty} \phi(\Delta) d\Delta - \frac{\partial \Phi(r, t)}{\partial r} \int_{-\infty}^{\infty} \Delta \phi(\Delta) d\Delta + \frac{1}{2} \frac{\partial^2 \Phi(r, t)}{\partial r^2} \int_{-\infty}^{\infty} \Delta^2 \phi(\Delta) d\Delta \quad (13)$$

Taking into account that $\int_{-\infty}^{\infty} \phi(\Delta) d\Delta = 1$ and setting

$$\lim_{d\tau \rightarrow 0} \frac{1}{d\tau} \int_{-\infty}^{\infty} \Delta \phi(\Delta) d\Delta = \frac{d\bar{r}}{dt} \quad \text{and} \quad \lim_{d\tau \rightarrow 0} \frac{1}{d\tau} \int_{-\infty}^{\infty} \Delta^2 \phi(\Delta) d\Delta = \frac{d\sigma^2}{dt} \quad (14)$$

where $\frac{d\bar{r}}{dt}$ is the average particle growth rate and σ^2 is the size distribution variance, we obtain

the differential equation for the PSD function $\Phi(r, t)$:

$$\frac{\partial \Phi(r, t)}{\partial t} = - \frac{d\bar{r}}{dt} \frac{\partial \Phi(r, t)}{\partial r} + \frac{1}{2} \frac{d\sigma^2}{dt} \frac{\partial^2 \Phi(r, t)}{\partial r^2} \quad (15)$$

This equation has solution:

$$\Phi(r, t) = A \exp\left(-\frac{(r - \bar{r})^2}{2\sigma^2}\right) \quad (16)$$

$$A = \frac{2N(t)}{\sqrt{2\pi\sigma^2} \left(1 + \operatorname{erf}\left(\frac{\bar{r}}{\sqrt{2\sigma^2}}\right)\right)}$$

where A is a normalizing parameter calculated under the condition that $\int_0^{\infty} \Phi(r, t) dr = N(t)$.

The values \bar{r} and σ in Equation (16) can now be correlated with $\langle r \rangle$ and $\langle r^2 \rangle$:

$$\langle r \rangle = \bar{r} + \sqrt{\frac{2}{\pi}} \frac{\sigma \exp(-\bar{r}^2/2\sigma^2)}{1 + \operatorname{erf}(\bar{r}/\sigma\sqrt{2})}$$

$$\langle r^2 \rangle = \bar{r}^2 + \sigma^2 + \sqrt{\frac{2}{\pi}} \frac{\bar{r} \sigma \exp(-\bar{r}^2/2\sigma^2)}{1 + \operatorname{erf}(\bar{r}/\sigma\sqrt{2})}$$

$$\text{At } \sigma/\bar{r} \leq 0.4, \sqrt{\frac{2}{\pi}} \frac{\sigma \exp(-\bar{r}^2/2\sigma^2)}{1 + \operatorname{erf}(\bar{r}/\sigma\sqrt{2})} \leq 0.007 \bar{r} \text{ and } \sqrt{\frac{2}{\pi}} \frac{\bar{r} \sigma \exp(-\bar{r}^2/2\sigma^2)}{1 + \operatorname{erf}(\bar{r}/\sigma\sqrt{2})} \leq 0.0036(\bar{r}^2 + \sigma^2).$$

Therefore, with a very good approximation, $\bar{r} \approx \langle r \rangle$ and $\sigma^2 \approx \langle r^2 \rangle - \bar{r}^2$.

To compare growth/coarsening behavior in different systems and/or at different conditions, a normalized particle size, $\rho = r/\bar{r}$, is generally used. For this quantity, the PSD function (Equation 16) is modified to:

$$\Phi(\rho, t) = A\bar{r} \exp\left(-\frac{(\rho-1)^2}{2(\sigma/\bar{r})^2}\right) \quad (17)$$

Figure 1 shows experimental particle size distributions for a number of alloy systems. These experimental data were collected in ref. [5] and are shown in the figure as open circles. The Lifshitz-Slyozov distribution function is shown in Figure 1 as a dotted line. It is highly non-symmetric, it does not predict particles with sizes larger than $1.5 \bar{r}$ and it does not fit well the experimental data. At the same time, the normal distribution function describes the experimental data rather well and it has flexibility to change the PDS width and height by assigning different σ/\bar{r} ratios.

Figure 2 shows experimental particle size distribution for Sn particles after coarsening for 40 hours in a Pb-Sn liquid [13]. Theoretical PSDs derived from different modern theories of the particle coarsening are also shown in this figure. These PSDs are non-symmetrical and their agreement with the experimental PSD is rather speculative. The blue dashed line is the normal distribution given by Equation (17) with $\sigma/\bar{r} = 0.4$, which agrees with the experimental data very well. There is a number of other examples showing experimental PSDs developed during particle growth and coarsening to be described by the normal distribution function [14,15,16,17,18,19,20,21], in agreement with our analysis.

In conclusion, our theoretical analysis of particle growth and coarsening, which includes stochastic flux, predicts normal distribution of the particle sizes, independent on the particle volume fraction (see Equations 16 and/or 17). This result agrees well with the numerous experimental data and it solves a mysterious problem related with a non-symmetrical size

distribution in earlier LSW approach. As we can see from the present analysis, taking into account a stochastic process of solute diffusion inside/from the particles adds an additional (diffusion) term in the differential Equation (15) for the PSD function. This stochastic process was ignored in the previous LSW theories, which led to an artificial requirement that the LSW PSD function and all its derivatives should go to zero above some finite value of the particle size; otherwise the integral of the LSW distribution function would be logarithmically divergent [1,2,3].

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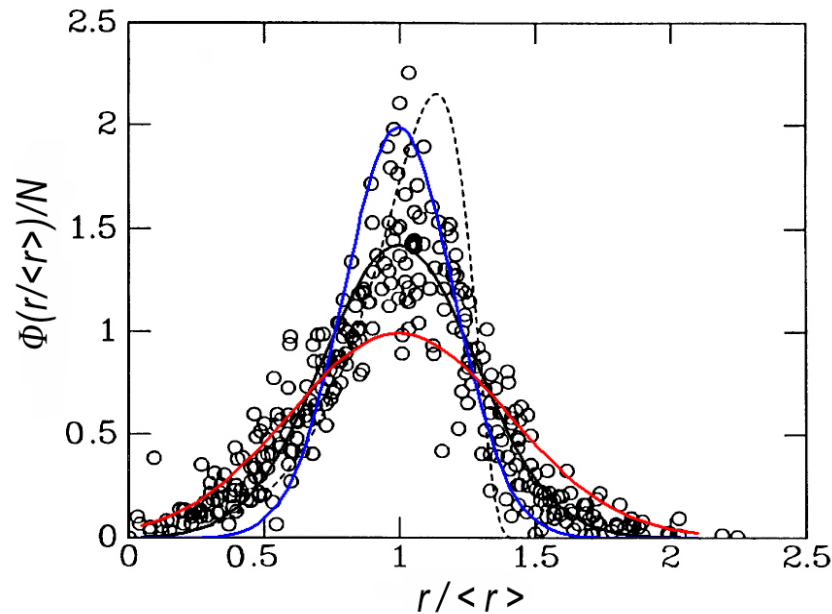


Figure 1. Experimental size distributions of growing particles in different alloy systems (shown as open circles and taken from Figure 1 of ref. [5]), Lifshitz and Slyozov distribution (dotted line) [3] and normal distributions (solid lines, Equation 17) at $\sigma/\langle r \rangle = 0.2$ (blue line), 0.28 (black line), and 0.4 (red line).

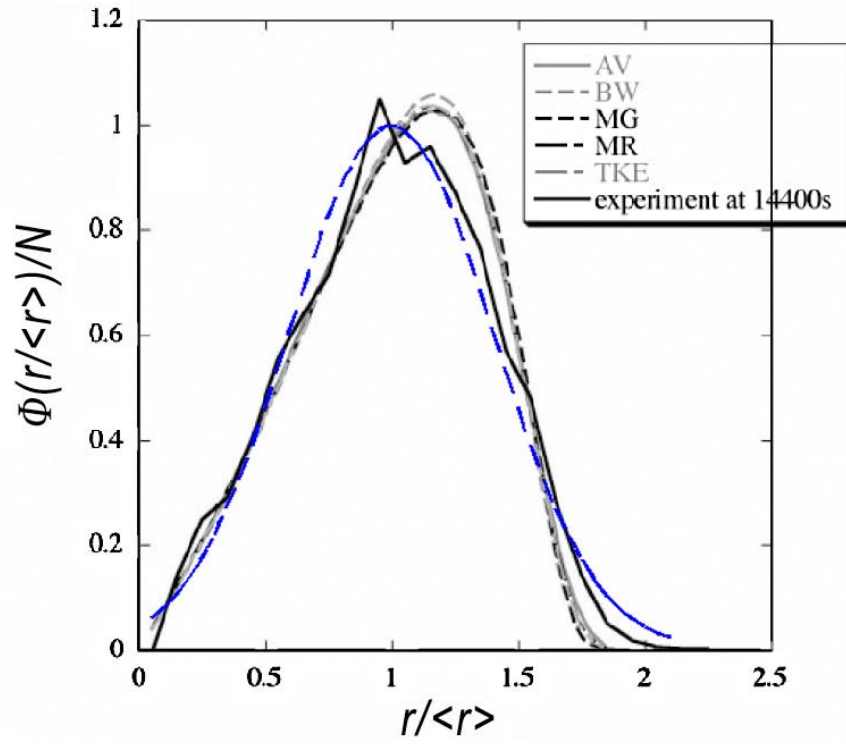


Figure 2. Experimental (dark solid line) and theoretical (other gray lines) particle size distributions for Sn particles by Snyder et al. [13]. The theoretical PSDs indicated in the legend are from modified LSW theories and the blue line

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